

by Constance Senior, Susan Thorneloe, Bernine Khan, and David Goss

**Constance L. Senior** is manager of engineering research and development at Reaction Engineering International, Salt Lake City, UT; **Susan A. Thorneloe** is a senior chemical engineer and **Bernine Khan** is a post-doctoral fellow, both with the U.S. Environmental Protection Agency's National Risk Management Research Laboratory, Research Triangle Park, NC; and **David Goss** is the former executive director of the American Coal Ash Association. He retired in February 2009. E-mail: [senior@reaction-eng.com](mailto:senior@reaction-eng.com).

# The Fate of Mercury

## Collected from Air Pollution Control Devices

Mercury that enters a coal-fired power plant originates from the coal that is burned and leaves through the output streams, which include stack emissions and air pollution control residues (either in solid or liquid form). This article describes recent findings on the fate and environmental stability of mercury in coal combustion residues (CCRs), such as fly ash and solid products from flue gas desulfurization (FGD) scrubbers, when either disposed or reused in agricultural, commercial, or engineering applications.



The major mercury-containing input to a power plant is coal.

New environmental regulations in the United States will result in lower mercury air emissions, but potentially more mercury in CCRs. The U.S. Clean Air Mercury Rule (CAMR) required the electric utility sector to remove at least 70% of the mercury released from power plant stack emissions by 2018. However, CAMR was vacated by the U.S. Court of Appeals D.C. Circuit in 2008. New rules are currently being worked on. According to the National Association of Clean Air Agencies, 20 states have implemented their own regulations already.<sup>1</sup> Other U.S. Environmental Protection Agency (EPA) regulations will necessitate the addition of new air pollution control devices for emissions of nitrogen oxides ( $\text{NO}_x$ ) and sulfur dioxide ( $\text{SO}_2$ ) at some power plants. This can also affect the fate of mercury in those plants.

### Pathways for Mercury in Coal-Fired Power Plants

The major mercury-containing input to a power plant is coal. The average mercury content in U.S. coals is 0.1  $\mu\text{g/g}$  (see Table 1).<sup>2</sup> Practically speaking, all mercury in the fuel is converted to elemental mercury vapor during coal combustion. As the flue gas cools, some of the elemental mercury may be oxidized. Both gaseous elemental and oxidized mercury can be adsorbed on suspended particles (fly ash), which consists of inorganic ash and unburned carbon. At the inlet of the air pollution control devices (APCDs), mercury can be found in the gaseous elemental ( $\text{Hg}^0$ ), gaseous oxidized ( $\text{Hg}^{2+}$ ), and particulate bound ( $\text{Hg}_p$ ) forms.

APCDs designed to capture  $\text{SO}_2$  and particulate matter (PM) can also remove mercury from flue gases in two ways: removal of  $\text{Hg}_p$  in particulate control devices and removal of  $\text{Hg}^{2+}$  in FGD scrubbers. Thus, the mercury removed from the flue gas may be found in fly ash and in the scrubber solids and liquid effluent.

The mercury that is removed in the FGD scrubber can partition to solid or liquid streams. Figure 1 illustrates the measured partitioning of mercury in FGD outlet streams at five pulverized-coal fired power plants.<sup>3</sup> The plants fired bituminous coals and had cold-side electrostatic precipitators (ESPs)

for particulate control. Each of these plants had a selective catalytic reduction (SCR) system for  $\text{NO}_x$  control and a wet FGD using calcium-containing slurry to control  $\text{SO}_2$ . Gaseous mercury removal by the FGDs ranged from 77% to 95%, and the mercury largely ended up in the scrubber solids.

Mercury appears to be concentrated in fine particles of scrubber solids that are predominantly iron oxyhydroxides, and is not strongly associated with the solid calcium sulfate in the scrubber.<sup>4,5</sup> In some wet FGD systems, the fine solids are recycled back to the scrubber after dewatering of the byproduct solid, while in others, they are disposed of, as was the case for two FGDs noted in a study by the Electric Power Research Institute.<sup>6</sup> Table 2 shows the distribution of mercury in the scrubber outlet streams for three limestone scrubbers in the study. For the two forced-oxidation scrubbers sampled, most of the mercury leaving the scrubber did so in the gypsum fines or fines liquor after the dewatering process. In forced oxidation scrubbers, this means that mercury can ultimately be in the gypsum fines, as well as in the FGD byproduct.

Dedicated mercury control technologies can be applied to plants to increase the amount of mercury removed from the flue gas. The most widely applied mercury control technology at coal-fired power plants is activated carbon injection (ACI). In the simplest application, all the activated carbon is collected with the fly ash generated by

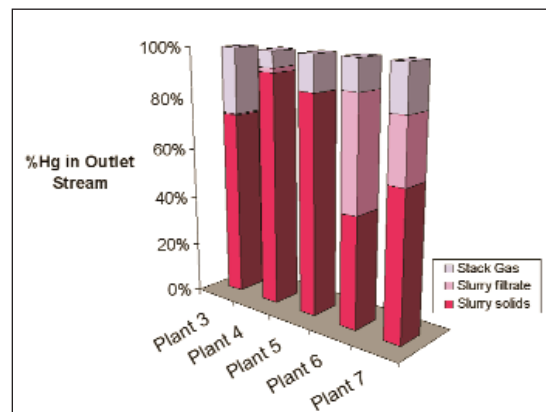


Figure 1. Distribution of mercury in FGD scrubber outflows at five bituminous coal-fired power plants with SCR and FGD.<sup>3</sup>

**Table 1.** Mercury content of fuel fired in power plants in 1999.<sup>2</sup>

Fuel Type	Number of Samples	Mercury Content (µg/g dry basis)	
		Mean	Range
Bituminous	27,793	0.11	0.0–1.3
Subbituminous	8180	0.07	0.008–0.9
Lignite	1047	0.11	0.02–0.75

**Table 2.** Distribution of mercury among scrubber outlet streams.<sup>6</sup>

Plant–Scrubber Type	FGD Byproduct <sup>a</sup>	Gypsum Fines <sup>b</sup>	Gypsum Fines Liquor <sup>c</sup>	Stack Gas
1 – Forced Oxidation	18.9%	7.8%	58.9%	14.4%
	7.3%	5.2%	65.6%	20.8%
2 – Forced Oxidation	48.1%	48.1%	0.0%	3.7%
3 – Inhibited Oxidation	65.7%			35.4%

*Notes:* <sup>a</sup>Calcium sulfate hemihydrate or gypsum produced by the FGD system; <sup>b</sup>Solid phase from hydroclone overflow stream sent to disposal; <sup>c</sup>Liquid phase from hydroclone overflow stream sent to disposal.

the plant, which results in a mixture of fly ash and spent sorbent that is higher in mercury than the fly ash alone. In some instances, a new fabric filter is added after the plant's existing PM control device, so that the activated carbon that is injected into the flue gas can be collected separately from the fly ash. This approach preserves the economic value of the fly ash by keeping it separate from activated carbon. The presence of activated carbon can impair one of the key uses of fly ash as a replacement of Portland cement in concrete (i.e., 14.5 million tons in 2007 or 26% of total amount of CCRs reused). Concrete-friendly activated carbons have been developed to alleviate this problem.

## Coal Combustion Residues

According to the American Coal Ash Association,<sup>7</sup> approximately 40% (i.e., 51 out of 126 million tons) of all CCRs produced in the United States are used in commercial or engineering applications to avoid land disposal. Figure 2 presents a summary of the primary uses by CCR type (e.g., fly ash, FGD gypsum, bottom ash). Of the 72 million tons of fly ash produced in 2007, 44% (32 million tons) was used in commercial applications such as making cement-related products, structural fill, and highway construction. Eight million tons of the FGD gypsum that was produced (or approximately 70%) was used in the making of wallboard. Figure 3

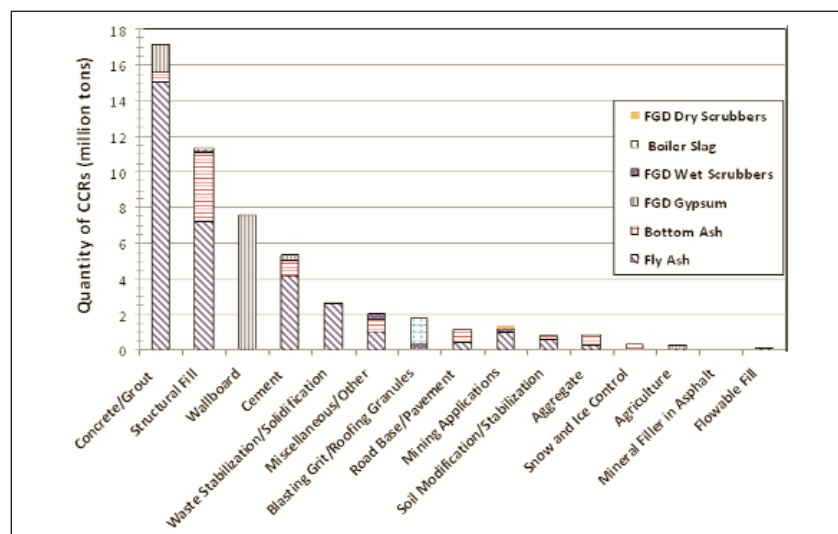
illustrates the wide range of mercury concentrations that have been found in fly ash (527 ng/g average, 16–1530 ng/g range) and FGD gypsum (512 ng/g average; 9–1110 ng/g range).<sup>8-10</sup>

## Stability of Mercury in Coal Combustion Residues

### Leaching Behavior of Mercury in CCRs

When there is no beneficial use for fly ash or FGD solids, they are often placed in landfills or ponds, where mercury (and other trace metals) might be leached out. Historically, single-point pH leaching

40% of all CCRs produced in the United States are used in commercial or engineering applications to avoid land disposal.



**Figure 2.** Distribution of CCR applications by CCR type.<sup>7,9</sup>

**Table 3.** Results of leach testing analysis for coal fly ash from six facilities using ACI for enhanced mercury capture.<sup>8</sup>

	Mercury	Arsenic	Selenium
Total in CCR material (mg/kg)	0.1-1	20-500	3-200
Leach results (µg/L)	Generally 0.1 or lower	<1-1000	5-10,000
MCL (µg/L)	2	10	50
TC (µg/L)	200	5000	1000
Variability relative to pH	Low	Moderate to High	Moderate

Notes: MCL = maximum concentration limit for drinking water; TC = toxicity characteristic and is a threshold for hazardous waste determinations; variability is defined as: low = <1 order of magnitude difference, moderate = 1 to 2 orders of magnitude difference, and high = >2 orders of magnitude difference.

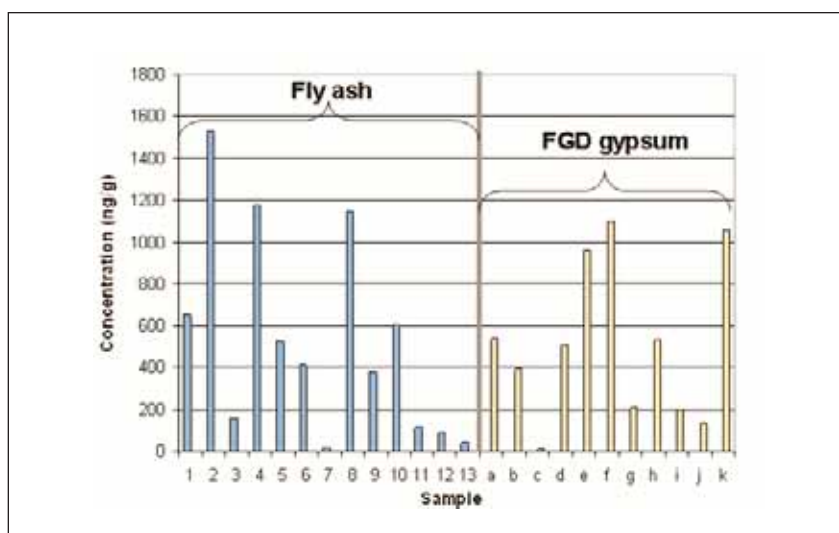
tests have been used to support CCR management decisions. EPA's Science Advisory Board<sup>8</sup> and the National Academy of Sciences<sup>11</sup> raised concerns over the use of single-point pH tests that do not reflect the actual conditions under which CCRs are typically managed. Because metal leaching rates change with changing environmental conditions (especially pH), the concern is that the existing leach tests being used for CCR management decisions may not be the most accurate predictor of potential environmental release of mercury or other metals.

In response to these concerns, EPA is using a more comprehensive leach testing framework<sup>12,14</sup> to investigate the potential for leaching of mercury and other metals from CCRs over the range of field conditions to which CCRs are typically exposed

to during land disposal and in engineering and commercial applications. The framework includes different test methods that consider: pH- and liquid-to-solid (LS) ratio-dependent leaching, percolation-based release using column testing, and diffusion-limited release from monoliths and compacted granular materials that behave as monoliths after placement. Public release of the draft methods is planned for fall 2009 as SW-846 Draft Methods.<sup>13</sup>

Using the pH-LS test method, CCRs are being collected from U.S. coal-fired power plants to span the range of coal types and APC configurations. In the first report released from this EPA research, fly ashes from six facilities with and without the use of sorbents for enhanced mercury capture were evaluated.<sup>8</sup> Table 3 provides results for mercury, arsenic, and selenium. The results show that mercury is strongly retained by the fly ash and unlikely to be leached at levels of environmental concern. However, there is potential concern for increased mobility of arsenic and selenium. A second report provides data for a wider range of metals from evaluation of 23 samples collected from eight facilities that use wet FGD scrubbers.<sup>9</sup>

Results for fly ash and FGD gypsum indicate that although there may not be a concern for leaching of mercury, other metals may be of concern (see Tables 4 and 5).<sup>9</sup> Results also suggest that there may be more of a concern in terms of potential leaching of metals for fly ash and scrubber sludge than for FGD gypsum. The blocks that are highlighted in Tables 4 and 5 indicate where there may be potential concern when comparing the leach



**Figure 3.** Mercury concentration in fly ash and FGD gypsum samples.<sup>8-10</sup>



results to health-based levels (i.e., MCL or TC). The use of these results are intended as inputs to groundwater transport and fate models, which take into account attenuation and other factors important in determining levels of potential concern to human health and the environment.

Figure 4 presents mercury leach testing results across the pH range for fly ash and scrubber sludge with and without the use of post-combustion NO<sub>x</sub> control. There appears to be an effect on the leaching behavior with the use of post-combustion NO<sub>x</sub> control. Additional information on the fate of mercury and other metals at plants using more stringent APCDs will be reported from EPA research program as part of the work outlined in the EPA Mercury Road Map.<sup>15</sup>

A third report is being drafted from analysis of 43 samples obtained from 16 facilities with multipollutant controls in use at coal-fired power plants. This report is expected to be released by spring 2010. A leaching assessment tool is being developed to provide easier access to the improved leach data for a range of CCRs and potential field conditions. The tool can also be used for data storage and viewing when using the new SW-846 leach test methods. The results from the leaching assessment tool are to provide more realistic leach data as input to future risk assessments and to help ensure protection of human health and the environment for future CCR management decisions.

#### Thermal Stability of CCRs

Some uses of CCRs may involve high-temperature

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processing that may increase the potential for release of mercury and other metals. In cement manufacturing, for example, CCRs may be raw feed for producing clinker in cement kilns. Virtually all mercury will be volatilized when CCRs are used as feedstock to cement kilns as the result of high operating temperatures (1450 °C).<sup>16</sup> EPA has proposed to reduce mercury emissions from cement kilns, which may result in the use of APCDs similar

**Table 4.** Leach data for fly ash.<sup>9</sup>

	Mercury	Arsenic	Selenium	Antimony	Barium	Boron	Cadmium	Chromium	Cobalt	Lead	Molybdenum	Thallium
Total in material (mg/kg)	0.04–0.6	70–90	2–30	3–15	600–1500		0.7–1.5	100–200	20–50	40–90	10–20	3–13
Leach results (µg/L)	<0.01–0.4	7–300	7–400	<0.3–200	90–4000	200–300,000	<0.2–30	1–4000	<0.3–200	<0.2–2	100–40,000	<0.3–300
MCL (µg/L)	2	10	50	6	2000	7000 DWEL	5	100		15	200 DWEL	2
TC (µg/L)	200	5000	1000		105	6500	1000	5000		5000		200
Variability relative to pH	Low to High	Low to Medium	Low to Medium	Medium to High	Low	Medium to High	High	Low to Medium	High	Medium	Low to Medium	Medium

*Notes:* MCL = maximum concentration limit for drinking water; TC = toxicity characteristic and is a threshold for hazardous waste determinations; DWEL = drinking water equivalent level; variability is defined as: low = <1 order of magnitude difference, moderate = 1 to 2 orders of magnitude difference, and high = >2 orders of magnitude difference. Shaded areas indicate potential for exceeding thresholds for MCL and TC.

**Table 5.** Leach data for FGD gypsum.<sup>9</sup>

	Mercury	Arsenic	Selenium	Antimony	Barium	Boron	Cadmium	Chromium	Cobalt	Lead	Molybdenum	Thallium
Total in material (mg/kg)	0.01–0.5	2–4	2–30	2–6	3–60		0.3–0.5	6–20	1–4	1–12	2–12	0.6–2
Leach results (µg/L)	<0.01–0.6	0.5–10	4–3000	<0.3–10	40–400	40–70,000	<0.2–50	<0.3–50	<0.2–10	<0.2–10	1–600	<0.3–20
MCL (µg/L)	2	10	50	6	2000	7000 DWEL	5	100	15	15	200 DWEL	2
TC (µg/L)	200	5000	1000		105	6500	103	5000	5000	5000		
Variability relative to pH	Low to Medium	Low to Medium	Low to Medium	Low	Low	Low to Medium	High	Medium to High	Low	Low	Low	Low

*Notes:* MCL = maximum concentration limit for drinking water; TC = toxicity characteristic and is a threshold for hazardous waste determinations; DWEL = drinking water equivalent level; variability is defined as: low = <1 order of magnitude difference, moderate = 1 to 2 orders of magnitude difference, and high = >2 orders of magnitude difference. Shaded areas indicate potential for exceeding thresholds for MCL and TC.

to those used at coal-fired power plants (e.g., wet scrubbers and sorbents for enhanced mercury capture).<sup>17</sup> The addition of APCDs at cement kilns should not affect the ability to use fly ash or FGD gypsum in the production of clinker. However, to avoid installation of APCDs, kiln inputs (e.g., fly ash) containing mercury may be avoided, which could impact usage of some CCRs.

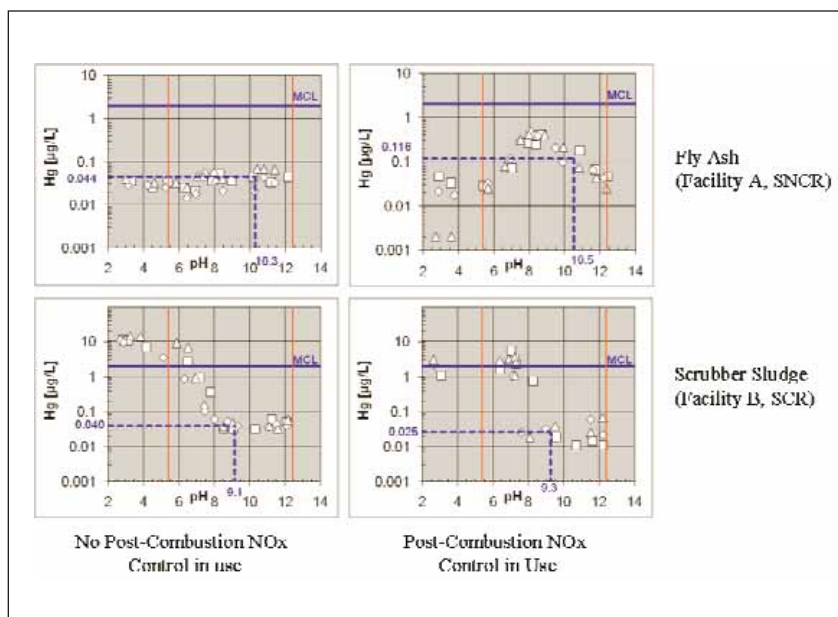
There has also been concern raised for other processes, such as the production of asphalt. Using 13 different CCRs, a laboratory simulation was conducted on asphalt production at 170 °C. The results suggest that volatilization of mercury is less

than 10% except for one CCR where results suggested volatilization of 92–100%.<sup>16</sup>

The best data available for thermal stability during wallboard production are from a study of five wallboard plants where a mercury mass balance was attempted.<sup>10</sup> Mercury loss was evaluated for surface drying, calciners, and board-line dryers. The wide variation in mercury loss (2–55%) from seven FGD gypsum samples was attributed to the different conditions under which each gypsum sample was generated. This variability included coal type, air pollution control configuration, and purge rate of fine gypsum particles.

Any remaining mercury in the finished FGD-wallboard could be released during use or subsequent disposal or recycling of the wallboard. Research is underway at EPA to evaluate the fate of mercury and other metals through each stage of the life cycle for FGD gypsum.

Curing of concrete can also involve elevated temperatures (80 °C). For a laboratory simulation experiment, mercury emissions were measured at 0.4–5.8 ng of mercury/kg of concrete for steam curing. The study reported mercury flux from exposed concrete surfaces to not exceed mercury fluxes from soils (4.2 ng m<sup>-2</sup>h<sup>-1</sup>). The study concluded that less than 0.022% of the total quantity of mercury present in concrete was released during the curing process. Therefore, greater than 99% of the mercury was retained in the concrete under the conditions tested.<sup>18</sup>



**Figure 4.** Leach data for mercury as a function of pH and comparison to health-based levels for fly ash and scrubber sludge.<sup>9</sup>

## Release of Gaseous Mercury from Landfills

There has been concern about the stability of mercury in fly ash or FGD waste when these materials are disposed in a landfill. Laboratory studies and field measurements of solid-gas exchange between fly ash and fly ash mixed with FGD solid mixtures have been conducted.<sup>19</sup> These studies have shown that fly ashes from bituminous and subbituminous coals act as a sink for atmospheric mercury, while lignitic fly ash may emit mercury to the atmosphere. In the field, mercury fluxes (solid to gas) from both uncovered and vegetated, topsoil-covered landfills containing bituminous or mixed subbituminous-bituminous fly ash were determined to be lower than the mercury fluxes from the surrounding soils. Mercury fluxes from a landfill containing FGD solids mixed with lignitic fly ash were estimated to be about four times higher than the surrounding soil.<sup>19</sup>

from the stack gas to fly ash, FGD gypsum and other air pollution control residues. This may have a significant impact on fly ash production and quality. For several commercial uses, it appears less likely that mercury in CCRs will be reintroduced into the environment, at least during the lifetime of the product. Based on measurements to date, mobilization of mercury in CCRs in ash landfills, from leaching or gaseous release, appears to be low. However, the impact of advanced mercury emissions control technology (e.g., ACI) on beneficial use applications is uncertain. There is concern that the presence of increased concentrations of mercury or certain other metals, or high carbon content may reduce the suitability of CCRs for use in some applications (e.g., carbon content can limit use as replacement for Portland cement or as concrete admixture). **em**

## Summary

The addition of FGD systems, SCR, ACI to capture mercury, SO<sub>2</sub>, and other pollutants will shift mercury

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